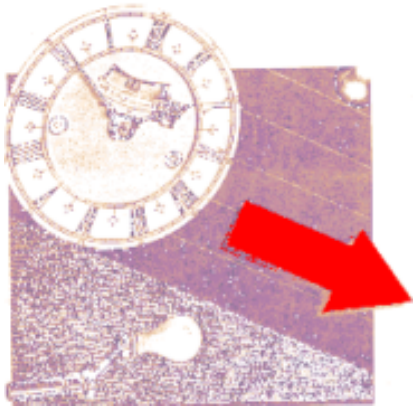
ENTROPY

"The second law of thermodynamics is time's arrow,
but chemical kinetics is time's variable clock."
-F.Lambert



"Chemical kinetics firmly restrains time's arrow
in the taut bow of thermodynamics
for milliseconds to millennia."
-F.Lambert

CAUSE ALWAYS PRECEDES EFFECT...

Alien Story Example;
How do we know time is moving *forward?*

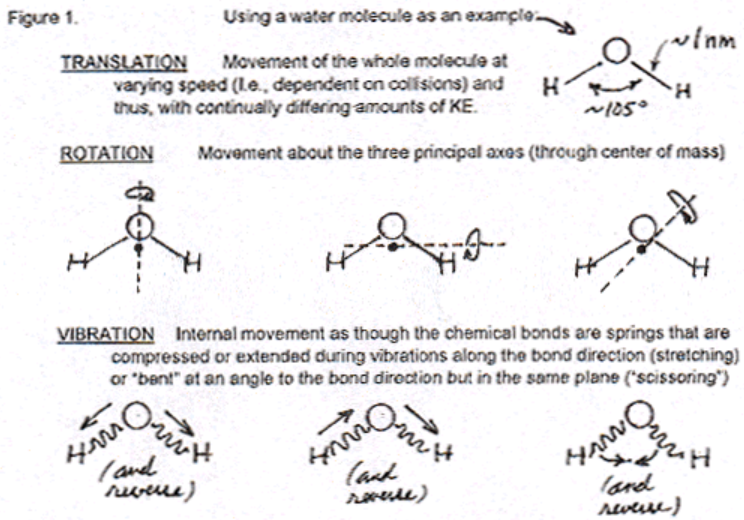
Spontaneous Reaction: A reaction that occurs naturally, without outside intervention.

**Remember, the reaction may take a LONG time (kinetics)!

** How does nature "decide" which procesess ought to be "spontaneous"? Entropy!

Entropy (ΔS): The capacity of a system to store dissipated ("spread out") energy.

Examples of Ways to Dissipate Energy:



Of the above types of energy, which types can a solid have?

A Gas?

A Crystal at 0 K?

Recording Energy Changes (ΔS_{system}): Entropy Final - Entropy Initial

- Positive = Storing more "dispersed energy" *after* change (more disorder)

Predict the sign on ΔS for the following changes:

1. Steam condenses.

2. A salt dissolves.

3. Iodine vapors condenses on a cold surface to form a crystal.

Review, What is the 1st Law of Thermodynamics?

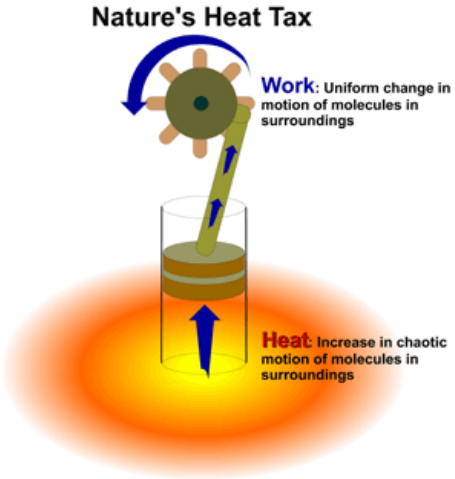
The 2nd Law of Thermodynamics: All spontaneous reactions result in an increase in entropy (energy disspersion) in the universe.

$$\Delta S_{universe} > 0$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

$$\Delta S_{surr} > - \Delta S_{sys}$$

Summary: 1st Law says you can't get ahead, 2nd Law says you can't even break even!



http://www.maniacworld.com/Laminar-Reverse-Flow.html

Summary

ΔS_{univ}	ΔS_{sys}	ΔS_{surr}	Spontaneous Reaction?
	−	−	
	−	+	
	+	−	
	+	+	

What about those reactions that "might be" spontaneous?

Spontaneity depends on the *temperature* at which the reaction occurs!

Example, Water Freezing - "Might Happen"

ΔH_{sys} ΔS_{sys}

ΔH_{surr} ΔS_{surr}

Does entropy *gained* by the surroundings offset the entropy lost by the system?

$\Delta S_{surr} > - \Delta S_{sys}$

Yes, if it's cold outside!

****Magnitude of entropy gained by surroundings depends on the temperature.**

$\Delta S_{surr} = - \Delta H_{sys} / T$ at constant T and P

When it's cold out, a little heat goes a long way!

Winning the lottery analogy....

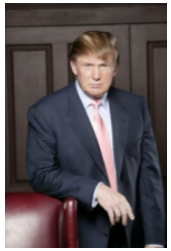
Cold Outside:

You, poor high school student + $1000 =

+ $1000 →

Hot Outside:

Donald Trump + $1000 =



+ $1000 →

Putting ΔH and ΔS together...

Gibbs' Free Energy: The energy available to do work.
At constant pressure and temperature….

$$\Delta G_{sys} = \Delta H_{sys} - T\ \Delta S_{sys}$$

related to 2nd Law...

All with respect to *system*

ΔS	ΔH	ΔG	Spontaneous?

Reactions are spontaneous when ΔG_{sys} _____

Reactions are at equilibrium when ΔG_{sys} _____